



# The photocatalytic activity and kinetics of the degradation of an anionic azo-dye in a UV irradiated porous titania foam

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## ABSTRACT

A porous organic–inorganic hybrid titania foam, prepared from a long chain organic surfactant, hexadecylamine (HDA) and a semiconductor powder was characterized by microscopic and spectroscopic techniques and photocatalytically evaluated for the solution phase decomposition of methyl orange under alkaline conditions. Kinetic data obtained indicate conformity with Langmuir–Hinshelwood kinetic model at the initial stages of the degradation reaction. An attempt was made to study the effect of experimental parameters including catalyst loading and dye concentration on photocatalytic degradation of MO. Results indicate that the rate of reaction is governed by adsorption of azo-dye into the surface of the photocatalyst materials and suggests an optimum catalyst load and dye concentration for the degradation reaction. Light absorption and scattering within the substrate reaction zone and arising from differences in optical properties of catalyst material, made it impossible to interpret entire kinetic data on the basis of a simple Langmuir–Hinshelwood kinetics. However, kinetic data obtained at the initial stages of the reaction suggest conformity with first-order kinetics. The foam promises to be a versatile material in that it can be used for the treatment of low concentrations of pollutants of biological, organic and inorganic origins in water and air.

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## 1. Introduction

Heterogeneous photocatalysis has emerged as an effective technique for the solution and gas-phase degradation of a host of pollutants of organic, biological and inorganic origins leading to the total mineralization of most organic pollutants and organic reactive dyes [1–10]. Due to its ability to degrade a variety of toxic organic compounds in air and water, TiO<sub>2</sub> remains the most frequently studied semiconductor heterogeneous photocatalyst. Many reviews of different aspects of single-crystalline metal oxide surfaces have been reported in recent years [11–14] and significant research efforts using a variety of analytical methods have been applied to study various TiO<sub>2</sub> surfaces [14–17]. For example, TiO<sub>2</sub> surfaces for films and particles have become model systems in the science of metal oxide surfaces because reduced TiO<sub>2</sub> single crystals are easy to work with and the growth morphology, interfacial oxidation and reduction reactions as well as thermal stability and geometric structure of the porous TiO<sub>2</sub> surface are the most critical parameters required for the reactivity of these materials [17].

The development of novel, well structured, porous, high surface area and complex forms of titanium dioxide is an area that is under intensive research [11]. For efficiency optimization reasons, the main parameter to be controlled is the nanostructure of the porous material. We report here the synthesis of a titanium dioxide foam, starting from a commercially available material, TiO<sub>2</sub> Degussa P-25 and a long chain organic surfactant and its application as a photocatalyst for the solution phase degradation of an industrial pollutant, methyl orange.

Textile and similar other industries produce large amounts of colored dye effluents which are toxic and in most cases, non-biodegradable. These effluents create major environmental problems if they release potentially harmful carcinogenic substances into the aqueous phase. As a result of this, various chemical and physical treatment processes have been advanced including precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration. These processes are non-destructive since they only transfer the non-biodegradable matter into sludge, giving rise to new problems which need further treatment [18–20].

Methyl orange, structure shown below, is an anionic azo-dye used in many process industries including dyeing, paper and pulp processing and printing textiles. It is a major water pollutant in these industries and the release of these dyes into the environment

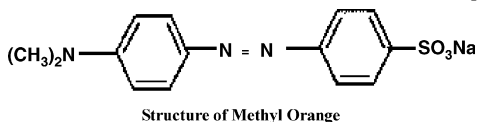
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usually create major problems and so there are intense research efforts aimed at the decolorization of these dyes [21–23]. The aim of this work was to study the catalytic activity of a porous titania foam for the decomposition of aqueous solutions of methyl orange under alkaline conditions. This would enable the identification of key parameters such as pore size, surface area and catalyst load that can be experimentally manipulated to control photoactivity and the decolorization reaction.

## 2. Experimental

The pollutant used in this work was a methyl orange, which has the formula (4-[[[(4-dimethylamino)phenyl]-azo]benzenesulfonic acid sodium salt) and molecular formula  $[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{SO}_3\text{Na}]$  or acid orange 52, shown below, was obtained from Merck and used without purification.



It is a stable compound and a typical azo-dye in the textile industry and the subject of previous studies [24]. Analytical grade hydrogen peroxide and acetylacetone were obtained from Fisher Scientific Ltd., UK. Hexadecylamine (HDA) was obtained from Fluka while Degussa P-25 was supplied by Degussa AG, Macclesfield, England. Double distilled water was used for the preparation of various experimental solutions. A detailed procedure for preparing the  $\text{TiO}_2$  foam is provided in [25]. The characterization of the foam, involving spectroscopic and diffractive measurements, has also been reported in earlier publications [25]. However, because of the relevance to the present study, the SEM measurements are discussed in the present study.

### 2.1. Photocatalytic studies

Titania foam is a promising material for environmental applications, for example, the deactivation of gas-phase organics as well as biological and inorganic pollutants. With respect to the decolorization of dyes, methyl orange was chosen for study as a model pollutant compound. To evaluate the catalytic activity of the titania foam towards MO degradation, photocatalysis experiments were conducted in a batch photoreactor used in previous studies consisting of round-bottomed photocatalytic pyrex glass cells cut-off wavelength 320 nm. Previous studies have indicated that this azo-dye was not decomposed even after prolonged periods of irradiation in the absence of a photocatalyst [26]. The photocatalytic activity was therefore expressed as a percentage of the disappearance of this pollutant in terms of the rate of decolorization and recorded as a change in intensity of the characteristic absorption peak of the dye.

To 150 ml of dye solution (pH 8), titania foam powder photocatalyst was added and the solution was subjected to irradiation. The radiation system used was equipped with two parallel F15 W/T8 UV light tubes which have a maximum emission at 350 nm. The radiation from the system was measured using a 28-0925 Ealing Research Radiometer-photometer operating in conjunction with a 28-0982 silicon detector and a 28-0727 flat response filter. Aqueous solutions of methyl orange containing different loads of the composite titania foam, specific surface area  $17.5 \text{ m}^2/\text{g}$  were photocatalysed. All solutions were  $\text{O}_2$  bubbled to achieve dissolved oxygen saturation and spectrophotometrical analytical determination was carried out at 465 nm ( $\text{MO} = 25,100 \text{ M}^{-1} \text{ cm}^{-1}$ ) while constant stirring was achieved using magnetic stirrers.

To determine the percentage of dye discolorization with time, aliquots were taken from the solution at different time intervals with a syringe and filtered through Millipore Syringe filter of  $0.45 \mu\text{m}$  and the absorption spectra was recorded. The rate of decolorization was determined from the change in intensity of  $\lambda_{\text{max}}$  of the MO. Initial pollutant concentration and pH were set at 5 mg/l and pH 8 as previous studies on methyl orange have indicated that the maximum rate of degradation of MO occurred at a pH of 8 [27–29] although the maximum adsorption of this anionic dye was at a pH of 4 [30]. A similar observation has been made by Hasnat et al. in a comparative photocatalytic study of the decolorization of an anionic and a cationic dye [31] as well as Guillard et al. [2] who in a study of the effect of pH on the degradation of several dyes, observed that the rate of degradation increased with pH and that the rate was higher in alkaline environments. The photocatalytic decomposition rate of MO was determined using the following equation [32,33]:

$$\text{photocatalytic decomposition rate} = \frac{C_0 - C}{C_0} \quad (1)$$

where  $C_0$  is the initial concentration of methyl orange solution and  $C$  is the final concentration after illumination by UV light. This enabled the determination of the decolorization efficiency (%) according to the following equation [34]:

$$\text{efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

## 3. Results and discussions

### 3.1. Characterization of titania foam

A scanning electron microscopy (SEM) image of the titania foam reveals a spongy, rough and porous microstructure. Low magnification image of the foam shows an extended network of features separated by large pores with a diameter of approximately 1–2  $\mu\text{m}$ . By increasing the SEM magnification, the fine texture of the foam features can be seen. No existence of grainy matter was observed, demonstrating that a complete reaction had occurred. The spongy porous structure of the foam enhances its ability to absorb photons and it is an important property of this material (Fig. 1).

### 3.2. Photocatalytic studies

Photocatalytic experiments were undertaken to evaluate the  $\text{TiO}_2$  foam as a material for water pollutant purification. To achieve this, various loads of the titania foam were evaluated for their

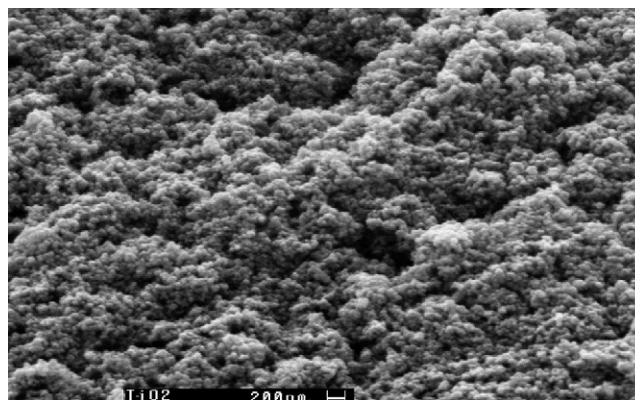


Fig. 1. Scanning electron microscopy image of a titania foam.

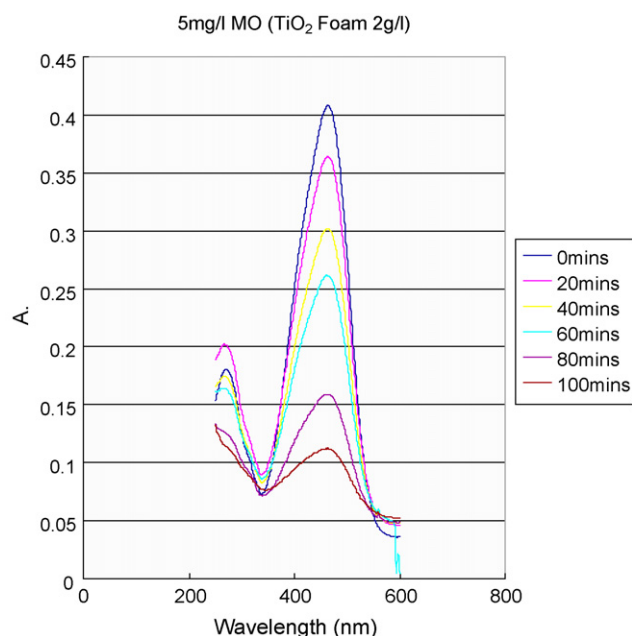
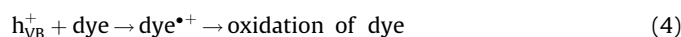
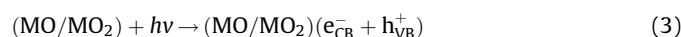


Fig. 2. Change in absorption intensity with time of methyl orange, pH 8.

catalytic activity towards methyl orange decomposition. The rate of decolorization was recorded with respect to the change in intensity with time of the absorption peak at 465 nm (Fig. 2). The absorption peak of the dye diminished with time and disappeared during the reaction indicating that the dye had been degraded. The photocatalytic decolorization of the dye in solution is initiated by photoexcitation of the semiconductor and the formation of electron hole pairs on the surface of the catalyst, Eq. (2). The high oxidative potential of the hole ( $h_{VB}^+$ ) in the catalyst allows the direct oxidation of the dye to reactive intermediates (Eq. (3)) according to the following reactions:



Another reactive intermediate that is responsible for the degradation is the hydroxyl radical ( $OH^\bullet$ ). The  $OH^\bullet$  radical is formed either by the decomposition of water according to Eq. (3) or by the reaction of a hole with  $OH^-$ , Eq. (4). The hydroxyl radical is a powerful non-selective oxidant with ( $E_0 = +3.06$  V) the use of which can lead to the partial or complete mineralization of a host of organic compounds in accordance with the following equations [35]:



The degradation kinetics of MO has been observed to conform to first-order kinetics [36–39] and it is well established that photocatalysis experiments follow the Langmuir–Hinshelwood model, where the reaction rate,  $R$ , is proportional to the surface coverage,  $\theta$ , according to the following equation:

$$R = \frac{-dc}{dt} = k_r \theta = \frac{k_r KC}{1 + KC} \quad (8)$$

where  $k_r$  is the reaction rate constant,  $K$  is the adsorption coefficient of the reactant and  $C$  is the reactant concentration.

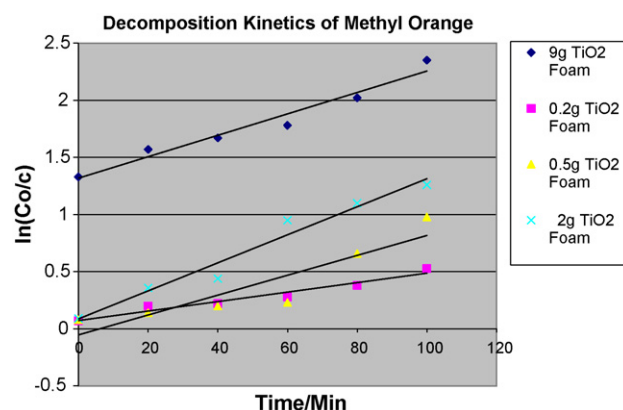


Fig. 3. First-order photodecomposition kinetics of MO, pH 8 in titania foam.

When  $C$  is very small,  $KC$  is negligible with respect to unity and Eq. (7) describes a first-order kinetics. The integration of Eq. (7) with the limit conditions that at the start of radiation,  $t = 0$ , the concentration is the initial one, and  $C = C_0$ , yields Eq. (8)

$$-\ln\left(\frac{C}{C_0}\right) = k_{app}t \quad (9)$$

where  $k_{app}$  is the apparent first-order rate constant. Fig. 3 shows the MO degradation kinetic data. The semi-logarithmic plot of the concentration data resulted in straight lines with a correlation constant varying between 0.9877 and 0.9766. A similar study obtained a value of 0.9836 and a rate constant of  $2.9 \times 10^{-4} \text{ s}^{-1}$  [31]. The photocatalytic rate was dependent on the amount of catalyst used, with percentage decomposition, measured as a decrease in methyl orange concentration (decrease in absorption peak), varying from 95.8% with 9 g of foam, 71.4% with 2 g of foam, 35.7% for 0.5 g of foam to 29% with 0.2 g of foam. After 100 min, a further increase in the irradiation did not result in a proportionate increase in the photocatalytic activity; the rate remained constant.

The data presented in Fig. 4(a) which shows the percentage decolorization using various amounts of catalyst, suggest that the rate of reaction is proportional to the initial concentration of catalyst in accordance with first-order kinetics. However, as the reaction progressed, this proportionality ceased to hold because after 100 min of irradiation, the 95.8% of decomposition achieved with 9 g of foam compared to 29% obtained with 0.2 g, represented only a 3.4-fold increase in decomposition and a 45-fold increase in catalyst load. In addition, a further increase in catalyst load did not result in a proportionate increase in photoactivity. In fact, the rate was unchanged.

The photocatalytic degradation of other organic compounds has also been observed to exhibit the same dependence on catalyst dose [40]. This has been explained on the basis that as the catalyst load increases, the turbidity of the solution increases resulting in a decrease in UV light penetration and the photoactivated volume [41]. This would either lead to a decrease in photocatalytic activity or no change at all if an optimum photocatalytic rate had already been achieved for a given catalyst load as explained earlier. On the other hand, Fig. 4(b) showing the amount of MO remaining undegraded with time as a function of catalyst load is another way of interpreting the data presented in Fig. 4(a). The rate of decolorization clearly depends on adsorption of the dye into the catalyst porous structure. The influence of pH on the photocatalytic efficiency of the foam is due to the amount of dye adsorbed on  $TiO_2$  [32]. This rate is fast at the beginning of the reaction as shown in Fig. 3 especially for high catalyst loads.

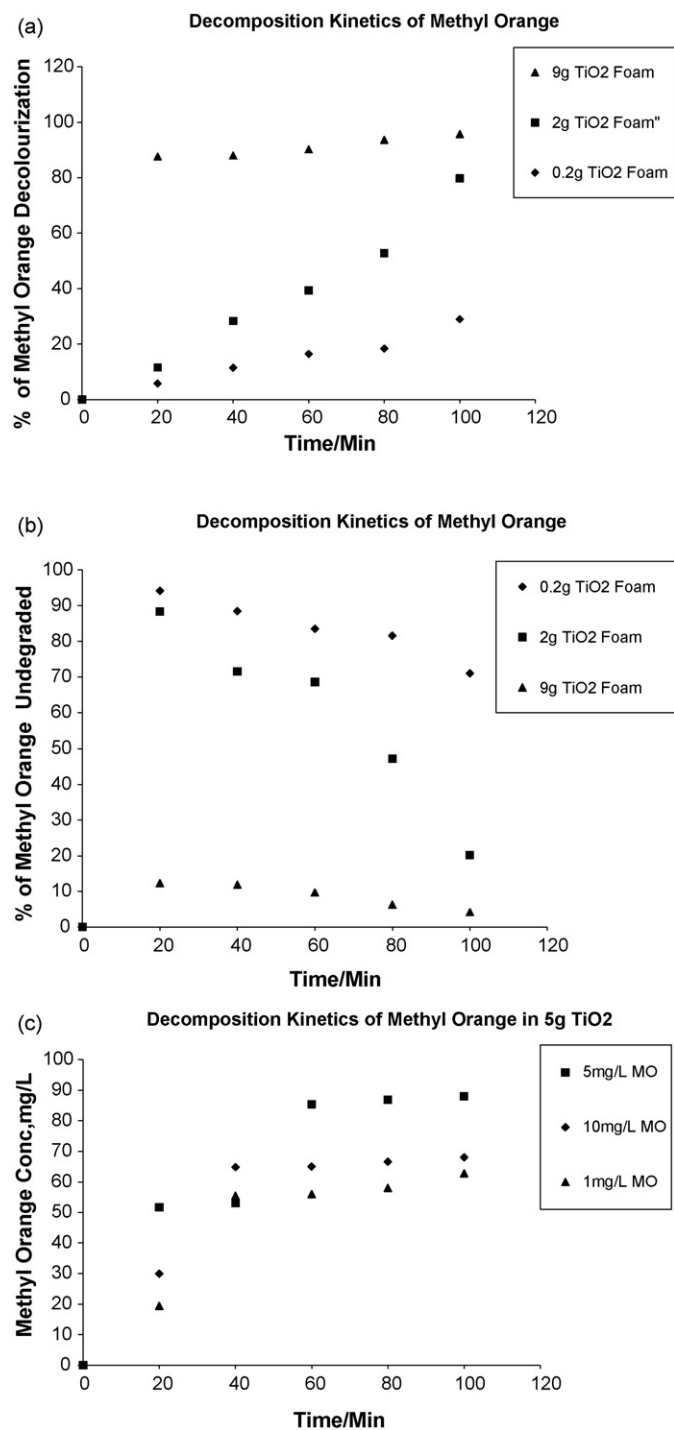


Fig. 4. Photodecomposition kinetics of MO, pH 8 in titania foam.

Dye concentrations of greater than 10 mg/l were also studied but no marked differences in the rate of degradation was observed. Actually, it was observed that the degradation efficiency decreased with increasing dye concentration (Fig. 4(c)). This has been observed in a similar study [42] in which results show that for dye concentrations of 5–10 mg/l, almost 100% complete degradation occurred within 60 and 120 min of irradiation. However, as the dye concentration was increased, the time for complete degradation increased significantly to 4 h using 25 mg/l concentration of methyl orange. A possible explanation for this is that as the initial

concentration of the dye increases, the path length of the photons entering the solution decreases leading to a slow down or decrease in photocatalytic efficiency and quantum yield. The same effect has been observed by Neppolian et al. [9] in a study of the degradation of three commercial textile dyes (reactive yellow, reactive red and reactive blue) using  $\text{TiO}_2$  photocatalysts. However, low concentrations of this dye, for example, 1 mg/l and below, are not suitable for this type of treatment.

These results although interesting, are based on the assumption that the catalyst particles were of the same size, had the same optical properties and were uniformly and equally illuminated. The kinetics will under these scenarios conform to the Langmuir–Hinshelwood model. However, it is now generally agreed that the Langmuir–Hinshelwood model holds only at the initial stages of the reaction where, in this case, the photocatalytic rate is governed by the adsorption of azo-dye onto the foam surface. As the reaction progresses, the  $KC$  term in Eq. (7) is no longer negligible and the kinetic data are no longer amenable to the simple Langmuir–Hinshelwood treatment.

A general and more appropriate approach to the analysis of photocatalytic data observed with the titania foam might be to develop a novel kinetic parameter/factor to explain the degradation efficiency per unit area of the catalyst. This treatment has been applied to many other similar cases [37]. This factor,  $K_{\text{surf}}$ , can be derived by dividing the apparent rate constant with the surface area of the catalyst as in Eq. (9).

$$K_{\text{surf}} = \frac{K_{\text{app}}}{S} \quad (10)$$

where  $K_{\text{surf}}$  ( $\text{min}^{-1} \text{cm}^{-2}$ ) is the novel parameter,  $K_{\text{app}}$  ( $\text{min}^{-1}$ ) the rate constant and  $S$  ( $\text{cm}^2$ ) the surface area of the photocatalyst.  $K_{\text{surf}}$  provides the net heterogeneous process efficiency, taking into account the area of the photocatalyst that can be utilized for decomposition processes. A  $K_{\text{surf}}$  value of  $0.376 \text{ min}^{-1} \text{cm}^{-2}$  calculated from Eq. (9) was obtained for the foam and compares with values obtained for other modified  $\text{TiO}_2$  materials [37–39]. These results suggest that the photocatalytic efficiency does not only depend on the amount of catalyst surface exposed to radiation, but also the type and nature of the exposed surface in terms of the chemical composition and micro-structural characteristics. This analysis although has been used widely [37] is subject to the assumption of uniformity of illumination of the entire catalyst surface.

The photocatalytic activity of commercial  $\text{TiO}_2$  (Degussa P-25) has studied and compared with modified  $\text{TiO}_2$  materials [37,38]. The modified materials were more efficient than the commercial  $\text{TiO}_2$ . For example, published work on studies carried out on methyl orange using pure titania, gold and silver modified titania materials, indicate that for the modified materials, the time to completely decolorize methyl orange was twice as fast as for pure  $\text{TiO}_2$ . In addition, the percentage degradation after 1 h of illumination was 34.5% for pure  $\text{TiO}_2$  compared to 90% for gold or silver modified  $\text{TiO}_2$ . The rate constant and time for complete decolorization were  $0.0103 \text{ min}^{-1}$  and 330 min for pure  $\text{TiO}_2$  [37–39]. In this study, the percentage degradation after 1 h of illumination was 47.15% for the  $\text{TiO}_2$  foam and the time for complete decolorization was 127.3 min (compared to 330 min and 34.5% for pure  $\text{TiO}_2$ ). Some authors, based on AFM, SEM, and XRD analysis alone, have suggested that the improved activity of modified  $\text{TiO}_2$  materials is due exclusively to improved surface properties [42]. A possible mechanism of decomposition of the azo-dye is given in Eqs. (4)–(6). However, further investigation is being carried out on the porosity and network architecture of the titania foam as well as on its mechanical stability.

#### 4. Conclusions

Further research into the mechanical stability of the foam as well as characterization of the network architecture and porosity are needed to fully quantify the photocatalytic activity of the TiO<sub>2</sub> foam. The X-ray diffractive measurements and SEM characterization of the titania foam show very rough and porous surfaces properties. These enhance the photocatalytic activity of TiO<sub>2</sub> foam towards methyl orange decomposition. The photocatalytic activity improved significantly with an increase in the amount of foam used as well as the time of radiation.

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